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C08F279/02(21)Application number : **05-133364**(71)Applicant : **DENKI KAGAKU KOGYO KK**(22)Date of filing : **03.06.1993**(72)Inventor : **TSUJI TSUYOSHI
SEKIYA TAKAYOSHI
KATO MASAYUKI****(54) PRODUCTION OF CHLOROPRENE GRAFT COPOLYMER**

(57)Abstract:

PURPOSE: To produce a chloroprene graft copolymer useful as an adhesive with slight discoloring.

CONSTITUTION: Chloroprene alone or a mixture of chloroprene and a monomer copolymerizable with chloroprene is polymerized in the presence of light-colored rosinic acid and/or a light-colored rosinate having &le;4 Gardner color scale in an alkali aqueous emulsion to give a chloroprene polymer, the chloroprene polymer is used as a trunk polymer and a (meth)acrylic ester is subjected to graft polymerization to give a chloroprene graft copolymer. In producing the chloroprene polymer as the trunk polymer, a mixture of a diethylhydroxylamine with a phenolic antioxidant is used as the polymerization terminator to produce the objective chloroprene graft copolymer.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture method of the chloroprene graft copolymer characterized by carrying out the graft polymerization of the acrylic ester (meta) by making into trunk polymer the chloroprene polymer obtained by carrying out the polymerization of the mixture of chloroprene independence or a chloroprene and a chloroprene, and the monomer that can be copolymerized to the bottom of four or less Gardner color standards existence of light color-ized rosin acid and/or light color-ized rosin acid chloride in alkaline water emulsified liquid.

[Claim 2] The manufacture method of the chloroprene graft copolymer according to claim 1 characterized by using the mixture of a diethylhydroxylamine and a phenol system antioxidant as a terminator on the occasion of manufacture of the chloroprene polymer which is trunk polymer.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the manufacture method of a chloroprene graft copolymer suitable as adhesives of materials, such as a polyvinyl chloride (the following, a plasticized polyvinyl chloride, and abbreviated name) containing a lot of still more detailed plasticizers, polyurethane, and nylon, about the manufacture method of a chloroprene graft copolymer with little coloring used as adhesives.

[0002]

[Description of the Prior Art] Manufacture of a chloroprene polymer is conventionally performed by carrying out the polymerization of the mixture of chloroprene independence or a chloroprene and a chloroprene, and the monomer that can be copolymerized in alkaline aqueous emulsified liquid.

[0003] Under the present circumstances, as an emulsifier, cation system emulsifiers, such as Nonion system emulsifiers, such as anion system emulsifiers, such as rosin acid chloride, an alkyl fatty-acid salt, and alkylbenzene sulfonates, or an alkyl polyethylene glycol, and polyvinyl alcohol, and also quaternary ammonium salt, etc. are used.

[0004] Especially, compared with the emulsifier of others [acid chloride / rosin], it has good film intensity at the time of the freezing dryness after a polymerization end, and it is known that too much contraction and breakage will not take place at the time of dryness. (Chemical Engineering Progress, 43(8), 391 (1947).) [0005] Therefore, in manufacture of a chloroprene polymer, it is most common to use rosin acid chloride as an emulsifier, and it is desirable.

[0006] A rosin acid is divided into the kind of disproportionation rosin made to dismutate a gum rosin, a wood rosin, tall oil rosin, or them by the difference in the manufacture method, and the polymer generated when which rosin acid was used, although use of all rosin acids was completed in manufacture of a chloroprene polymer is colored brown from yellow.

[0007] Moreover, in manufacture of a chloroprene polymer, if conversion is enlarged too much, in order to generate an insoluble component to an organic solvent and to spoil the physical properties of the obtained chloroprene polymer, it is the stage which carried out the polymerization to predetermined conversion, and it is common to add a terminator and to stop a polymerization.

[0008] As a terminator for stopping a polymerization, although a phenothiazin, a tetraethylthiuram disulfide, etc. are used, for example, the polymer generated too may color by the coloring component contained in these.

[0009] On the other hand, in using as adhesives, such as adhesives, especially a plasticized polyvinyl chloride, a graft reaction is carried out with methyl methacrylate in the organic solvent by using a chloroprene polymer as a raw material, and it makes it a graft copolymer.

[0010]

[Problem(s) to be Solved by the Invention] Thus, as for the manufactured graft copolymer for adhesives, it is common that the influence of the colored chloroprene polymer colors, and it has the following problems.

[0011] For example, when used for the shoes manufacture which used the plasticized polyvinyl chloride, it is mainly used for adhesion of the shoes upper part and a sole, and in the conventional chloroprene system graft copolymer, since adhesives are coloring, a glue line will be conspicuous, and appearance of a product will be worsened. Moreover, when used in addition to the use of shoes manufacture, it happens that it is the same as that of this, and the appearance of a product becomes bad. Since it was such, no coloring-ization of the above-mentioned adhesives was desired.

[0012] this invention succeeds in manufacturing a chloroprene graft copolymer with little coloring, as a result of inquiring wholeheartedly for the purpose of solution of this trouble.

[0013]

[Means for Solving the Problem] this invention namely, the mixture of chloroprene independence or a chloroprene and a chloroprene, and the monomer that can be copolymerized A polymerization is carried out to the bottom of four or less Gardner color standards existence of light color-ized rosin acid and/or light color-ized rosin acid chloride in alkaline aqueous emulsified liquid. It is the manufacture method of the chloroprene graft copolymer characterized by carrying out the graft polymerization of the acrylic ester (meta) by making the obtained chloroprene polymer into trunk polymer. Moreover, on the occasion of manufacture of the chloroprene polymer which is trunk polymer, it is related with the manufacture method of the above-mentioned chloroprene graft copolymer characterized by using the mixture of a diethylhydroxylamine and a phenol system antioxidant as a terminator.

[0014] In this invention, although coloring of a manufacturing [using the chloroprene polymer used and manufactured as a

raw material]-to emulsifier-light color-ized rosin acid/or light color-ized rosin acid chloride chloroprene system graft copolymer is improved greatly, a graft copolymer with still less coloring is obtained by using the chloroprene polymer manufactured using the terminator which used the diethylhydroxylamine and the phenol system antioxidant as the component as a terminator further as a raw material.

[0015] There are especially no restrictions as a chloroprene and a monomer which can be copolymerized, for example, 2, 3-dichloro-1,3-butadiene, 1-chloro-1,3-butadiene, a butadiene, an isoprene, styrene, acrylonitrile, an acrylic acid and its ester, a methacrylic acid, and its ester are mentioned, and if needed, two or more sorts may be combined and you may use.

[0016] If it is generally used to manufacture of a chloroprene polymer as a molecular weight modifier, there is especially no limit, for example, it can use well-known chain transfer agents, such as dialkyl xantho gene disulfide, such as long-chain alkyl mercaptan, such as n-dodecyl mercaptan and a tert-dodecyl mercaptan, diisopropyl xantho gene disulfide, and diethyl xantho gene disulfide, and iodoform.

[0017] Light color-ized rosin acid and/or light color-ized rosin acid chloride is used for the emulsifier kicked to this invention. The light color-ized rosin acid used here processes usual rosin acid soap with distillation, a column chromatography, etc., removes a coloring component, and makes it 4.0 or less Gardner color standards. Moreover, although light color-ized rosin acid chloride is a salt of a light color-ized rosin acid and an alkali-metal salt, an alkaline-earth-metal salt, an ammonium salt, etc. are raised, sodium salt and potassium salt are usually used suitably.

[0018] It is the same as that of the case of the usual rosin acid, and generally the amount of the light color-ized rosin acid and/or light color-ized rosin acid chloride used is converted per all monomer 100 weight sections and into a rosin acid, and its use about 0.1 - 10 weight section is desirable.

[0019] Although combined use of the usual rosin acid is not desirable at this time since coloring takes place to the product obtained, combined use of emulsion stabilizer, such as emulsifiers, such as a fatty acid and an alkylbenzene sulfonic acid, and sodium salt of the condensate of a naphthalene sulfonic acid and formaldehyde, is a book.

[0020] Although the same method as the case where a general chloroprene polymer is manufactured is sufficient as a polymerization method, as for polymerization temperature, it is desirable to carry out in 0-55 degrees C.

[0021] The organic or inorganic peroxide used by the emulsion-polymerization method of the usual chloroprene as a polymerization initiator, for example, a benzoyl peroxide, potassium persulfate, an ammonium persulfate, etc. are used.

[0022] Although the halt agent usually used, for example, a phenothiazin, a tetraethylthiuram disulfide, etc. may be used as a terminator in this invention, in order to acquire a higher light color-ized effect, it is desirable to use the mixture of a diethylhydroxylamine and a phenol system antioxidant.

[0023] As a phenol system antioxidant used by this invention, for example, 2, 6-G tert-butyl-4-methyl phenol, 2, 6-G tert-butyl-4-ethylphenol, a monochrome (alpha-methyl benzyl) phenol, A JI (alpha-methyl benzyl) phenol, a TORI (alpha-methyl benzyl) phenol, A 2 and 2'-methylene screw (4-ethyl-6-tert-butylphenol), A 2 and 2'-methylene screw (4-methyl-6-tert-butylphenol), 4 and 4'-butylidenebis (3-methyl-6-tert-butylphenol), 4 and 4'-thio screw (3-methyl-6-tert-butylphenol), 2, 5-G tert-butyl hydroquinone, 2, and 5-G tert-amyl hydroquinone etc. can be used. [0024] In this invention, the graft copolymer for adhesives with little coloring can be obtained by using a chloroprene polymer with little coloring manufactured by doing in this way as a raw material. Except using a chloroprene polymer with little coloring as a raw material, it cools in the place which it was the same as that of the usual method, was good, dissolved the few chloroprene polymer and few acrylic ester (meta) of coloring into the organic solvent, was made to add, warm and carry out the graft reaction of the polymerization initiator, measured the viscosity of a polymerization solution, and reached predetermined viscosity, and the manufacture method of a graft copolymer stops a polymerization.

[0025] As an acrylic ester used by this invention (meta), it can illustrate methyl-acrylate (meta), ethyl-acrylate (meta), butyl-acrylate (meta), and acrylic-acid (meta) 2-ethylhexyl etc. Even if it uses it independently, according to the purpose, you may use them, combining two or more sorts of these (meta) acrylic esters.

[0026] It is good that carrying out 30-120 weight section use carries out 50-100 weight section use of the acrylic ester at best still more preferably to the chloroprene polymer 100 weight section (meta) as manufacture prescription of the above-mentioned graft copolymer for adhesives. If fewer than 30 weight sections, the bond strength to a material will become inadequate, if [than the 120 weight sections] more, viscosity elevation of the reaction solution in a graft reaction will become intense, and control of a polymerization will become difficult.

[0027] As an organic solvent used at this graft reaction, ester, such as ketones, such as aromatic system hydrocarbons, such as benzene, toluene, and a xylene, a methyl ethyl ketone, methyl isopropyl ketone, and a methyl isobutyl ketone, ethyl acetate, and butyl acetate, is used as independent or a mixed solution. [0028] As a polymerization initiator, various kinds of radical initiators, for example, an azobisisobutyronitril, lauroyl peroxide, benzoyl peroxide, etc. can be used, and use of benzoyl peroxide is desirable especially. And the amount of the initiator used is used more than the 0.1 weight section to the graft-ized monomer 100 weight section. Moreover, since molecular weight regulation is performed, a suitable chain transfer agent can also be used.

[0029] It is necessary to perform reaction temperature above the decomposition temperature of the initiator to be used, and it is usually performed at 60-100 degrees C. Moreover, addition of the quinones which have the stabilization effect of a polymerization solution at the time of a polymerization end obtains good storage stability.

[0030] Thus, although the obtained chloroprene graft copolymer may be used as adhesives as it is, you may add the binder usually used according to the purpose of use, a stabilizer, other elastomers, etc.

[0031]

[Example] An example explains this invention in more detail below.

[0032] You distilled usual rosin acid soap for 4000g of chloroprene monomers with 10g n-dodecyl mercaptan, and made it emulsify using the reactor of 10l. of example of manufacture 1 content volume with a light color-ized rosin acids [of Gardner color standards 3 which obtained by performing removal of the low-boiling component which is a coloring component, and a high-boiling component / 12g and 3g] sodium hydroxide, and 4800g distilled water, and the polymerization was performed at 10 degrees C under nitrogen-gas-atmosphere mind, using potassium persulfate as an initiator. The emulsion of a phenothiazin was added in the place where conversion reached to 70%, and the polymerization was suspended. The unreacted monomer was removed by the steam stripping method of a conventional method, and the chip of a chloroprene polymer was obtained from the obtained latex by the freezing drying method of a conventional method. And color tone inspection was conducted about the chip of this chloroprene polymer with the Z-80 colorimetry color difference meter made from Nippon Denshoku Industry.

[0033] Except having used the mixture of a diethylhydroxylamine and a 4 and 4'-thio screw (3-methyl-6-tert-butylphenol) as example of manufacture 2 terminator, the polymerization was performed like the example 1 of manufacture, the chip of a chloroprene polymer was created and color tone inspection was conducted.

[0034] Chip 100g of the chloroprene polymer obtained in the example 1 of manufacture was dissolved in toluene 600g using the reactor of 1l. of example 1 content volume, methyl methacrylate 50g was added, the benzoyl peroxide was used for the initiator, graft polymerization was performed at 85 degrees C for 5 hours, and the chloroprene graft copolymer was obtained. And color tone inspection was conducted about this chloroprene graft copolymer with the Z-80 colorimetry color difference meter made from Nippon Denshoku Industry.

[0035] The chloroprene graft copolymer was created by the same method as an example 1 using the chip of the chloroprene polymer obtained in the example 2 of example 2 manufacture, and color tone inspection was conducted.

[0036] Except having used the disproportionation rosin acid (the Arakawa chemistry company make : RONJISUR) of Gardner color standards 10 for example of manufacture comparison 1 emulsifier, the polymerization was performed like the example 1 of manufacture, the chloroprene polymer was obtained and color tone inspection was conducted.

[0037] The chloroprene graft copolymer was created by the same method as an example 1 using the chip of the chloroprene polymer obtained in the example 1 of example of comparison 1 manufacture comparison, and color tone inspection was conducted.

[0038] The result of color tone inspection of the chloroprene graft copolymer which created the result of color tone inspection of the rubber chip compounded in the examples 1 and 2 of manufacture and the example 1 of manufacture comparison in examples 1 and 2 and the example 1 of comparison in Table 1 again is shown in Table 2.

[0039]

[Table 1]

表 1

サンプル	製造例		製造比較例 1
	1	2	
色調 ¹⁾	無色	無色	薄い褐色
N	5.2	-0.9	22.6
WB	54.3	61.2	41.2

1) N : The degree of yellow. It is WB:whiteness degree with strong yellow, so that this numeric value is large. There is so little coloring that this numeric value is large. [0040]

[Table 2]

表 2

サンプル	実施例		比較例 1
	1	2	
色調 ¹⁾			
N	14.9	16.1	29.9
WB	49.3	43.2	38.2

1) N : The degree of yellow. It is WB:whiteness degree with strong yellow, so that this numeric value is large. There is so little coloring that this numeric value is large. [0041]

[Effect of the Invention] this invention is as above the outstanding method of manufacturing a chloroprene graft copolymer

suitable as adhesives with little coloring.

[Translation done.]

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DERWENT-WEEK: 200325

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TITLE: Prepn. of chloroprene-graft
copolymer - comprises copolymerising (meth)acrylate(s) in
presence of chloroprene polymer as backbone

PATENT-ASSIGNEE: DENKI KAGAKU KOGYO KK[ELED]

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BASIC-ABSTRACT:

Prepn. of a graft copolymer comprises of copolymerising (a)
(meth)-acrylates in
presence of (b) the chloroprene polymer as the back-bone
polymer. The polymer
(b) is obtd. by polymerising (i) chloroprene or (ii)

chloroprene and
copolymerisable monomers, in presence of pale-yellowed
rosic acid with the
Gardner colour scale number of below 4 and/or pale-coloured
rodic acid salt, in
aq. alkali emulsion.

Also claimed is a process to produce the chloroprene
polymer, comprising that a
mixt. consisting diethylhydroxylamine and phenol type
stabilisers is used as a
polymerisation-stopping agent.

The polymerisation of chloroprene is carried out at 0-55
deg.C. The content of
the rosic acid ranges 0.1-10 pts.wt. based on 100 pts.wt.
of the total amounts
of the monomers.

ADVANTAGE - The graft copolymer gives adhesive adapted for
soft polyvinyl
chlorides, polyurethanes or polyamides esp.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: PREPARATION CHLOROPRENE GRAFT COPOLYMER
COMPRISE COPOLYMERISE
 METHO ACRYLATE PRESENCE CHLOROPRENE POLYMER
BACKBONE

DERWENT-CLASS: A12 A81 G03

CPI-CODES: A02-C; A04-B08; A04-F06E6; A10-C03B; G03-B02B;
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Polymer Index [1.2]

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